Resonant Inelastic Soft-X-ray-Scattering from DyF$_3$

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INTRODUCTION

For highly correlated materials, such as rare-earth compounds, studies of low-energy electronic excitations (intra-ionic f-f excitations in this case) can provide a better understanding of ground state properties. In the case of weak hybridization effects, the interlevel coupling and consequently *J*-mixing in the ground state of the system are often disregarded in the interpretation of experimental data by applying a pure atomic approximation (mainly for high-energy spectroscopies) or by using a first order crystal-field theory where the crystal field interaction is assumed to act only within the separate *J* manifolds. This is partly due to complications in extracting information about the ground state *J*-mixing directly from the data. For example, the estimation of the *J*-mixing degree in high-order crystal-field theory by adjusting the crystal-field parameters from the fit of optical absorption or low-energy electron-energy-loss spectra [1,2] may result in a large uncertainty originating from difficulties calculating the intensities of dipole-forbidden transitions. In turn, the possible influence of weak metal-ligand hybridization is difficult to analyze quantitatively in the absence of so-called charge-transfer satellites in high-energy spectroscopic data.

In this situation, the use of alternate spectroscopic means to obtain *J*-mixing information is essential. Recently, Finazzi et al. [4] have shown that the ground-state *J*-mixing can be studied by taking advantage of dichroic properties of rare-earth 3d x-ray absorption. However, the method is restricted to magnetically ordered systems. In this report we discuss the potential of resonant valence-to-core x-ray fluorescence spectroscopy (RXFS) to detect the ground-state *J*-mixing when applied to compounds without distinct long-range magnetic order and significant metal-ligand hybridization.

Similar to optical absorption and electron-energy-loss spectroscopies with respect to probing the low-energy excitations in electron-correlated materials, RXFS at the same time provides the higher level of the transition selectivity due to the element specificity and dipole selection rules. In contrast to systems with the strong metal-ligand hybridization where the charge-transfer process leads to an appearance of additional intense lines in resonant x-ray fluorescence spectra [5] as a result of inter-ionic excitations, *J*-mixing in systems with weak hybridization effects is expected to manifest itself in an intensity gain of some intra-ionic (f-f) transitions which are disallowed for the pure Hund-rule ground state. In other words, transitions with ΔJ other than 0, ± 1, and ± 2 are probed in the resonant excitation-deexcitation process (speaking correctly *J* is not a good quantum number in this case).

EXPERIMENTAL DETAILS

DyF$_3$ (99.99%) was congruently evaporated from a water-cooled effusion source in a simple preparation chamber utilizing a graphite crucible evaporator. The DyF$_3$ film (28 Å) was grown on ambient high purity platinum foil substrate at 4 x 10^{-9} Torr. The evaporation rate was calibrated by a quartz crystal monitor and the film thickness is estimated to be within about 10%. The film was stored under a nitrogen atmosphere and then loaded into the experimental chamber equipped with a
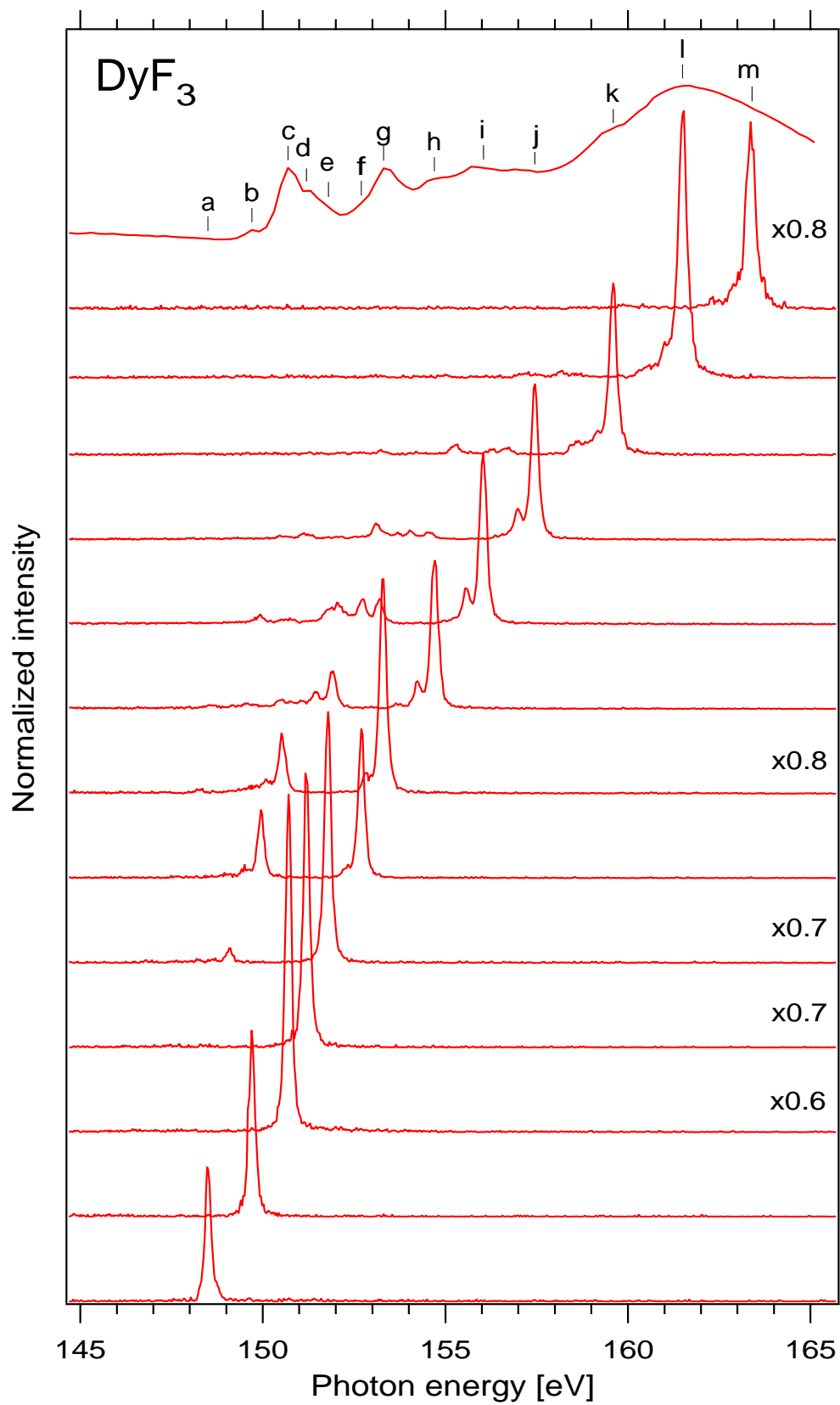
Figure 1. Total electron yield spectrum at the Dy 4d edge and resonant Dy 4f → 4d x-ray fluorescence spectra of DyF$_3$ normalized to the incoming photon flux. The letters correspond to the excitation energies indicated in the absorption spectrum.

fluorescence spectrometer. The sample was mounted with its surface normal located in the horizontal scattering plane.

The experiment was carried out at beamline 7.0 of the Advanced Light Source, Lawrence Berkeley National Laboratory with a spherical grating monochromator. The Dy 4f → 4d x-ray fluorescence spectra of DyF_3 were recorded using a grazing-incidence grating spectrometer [6] with a two-dimensional detector. The spectrometer resolution was set to 95 meV at 152 eV. The incidence angle of the photon beam was about 2˚ from the sample surface and the spectrometer was placed in the horizontal plane at an angle of 90˚ with respect to the incidence beam. To determine the excitation energies, the Dy 4d x-ray absorption spectrum of DyF_3 was obtained by measuring total electron yield at the 90˚ incidence angle of the incoming radiation. During x-ray absorption and fluorescence measurements, the resolution of the monochromator was set to 76 meV at a photon energy of 152 eV. All of the spectra were recorded at room temperature.

RESULTS AND DISCUSSION

The resonant Dy 4f → 4d x-ray fluorescence spectra of DyF_3 (Fig. 1) show a dispersion-like behavior upon tuning the excitation energy across the Dy 4d absorption edge. The spectra recorded at the excitation energies labeled by *a*, *b,* and *c* appear as a single peak with other low-energy structures being very weak. Further increase in the excitation energy gives rise to an enhancement of these weak structures so that the appreciable spectral weight is observed within the 8.5 eV range below the elastic line, for example, in spectra *i* and *j*. All of the low-energy peaks follow varying excitation energies and therefore can be associated with resonant inelastic x-ray scattering. It is rather unlikely that the spectral weight on the low-energy flank of the elastic line originates from phonon relaxation because this weight consists of distinct structures instead of a continuous structureless band and the structures show different dependence on the excitation energy.

There are two distinct groups of pronounced inelastic-scattering peaks in Fig. 1. The first group is distinguished by small energy losses on the tail of the elastic line, whereas the second is characterized by energy losses more than 2.5 eV. When the excitation energy approaches the main broad maximum of the Dy 4d absorption edge, the first group still possesses significant intensity while the structures of the second group become relatively faint. Regarding the energy scale on which the spectral variations occur, the observed fluorescent transitions can be attributed to intra-ionic f-f excitations. The energy gap between two groups of inelastic x-ray scattering structures reflects the separation between sextuplets and quadruplets of trivalent Dy [7,8] which can be reached due to the excitation-deexcitation process.

The results of preliminary atomic-multiplet calculations for the Dy^{3+} ion show that the dominant elastic peak in all of the Dy 4f → 4d spectra from DyF_3 is to large extent a consequence of strong interference effects in the intermediate state of the coherent second-order optical process. The states constituting the main 4d absorption edge have a lifetime broadening of about 2 eV largely because of the 4d-4f4f Coster-Kronig decay.

A close inspection of experimental 4f → 4d spectra shows that there are some spectral structures which are not revealed in calculations within the pure atomic approximation. Thus, the feature with the energy loss of about 1.15 eV is observed in spectra *h*, *k*, and *l*, presented in detail by Fig. 2. While atomic multiplet theory predicts the non-zero intensities for resonant inelastic x-ray scattering transitions to the $^6H_{13/2}$, $^6H_{11/2}$, and $^6F_{11/2}$ sextuplets of the $4f^9$ configuration, the energy of the extra-feature in experimental spectra *h*, *k*, and *l* (Fig. 2) is close to those of $^6F_{9/2}$ and $^6H_{7/2}$ manifolds of Dy^{3+} in LaF_3 [9]. This is an indication of *J*-mixing and the presence of $J = 13/2$ and
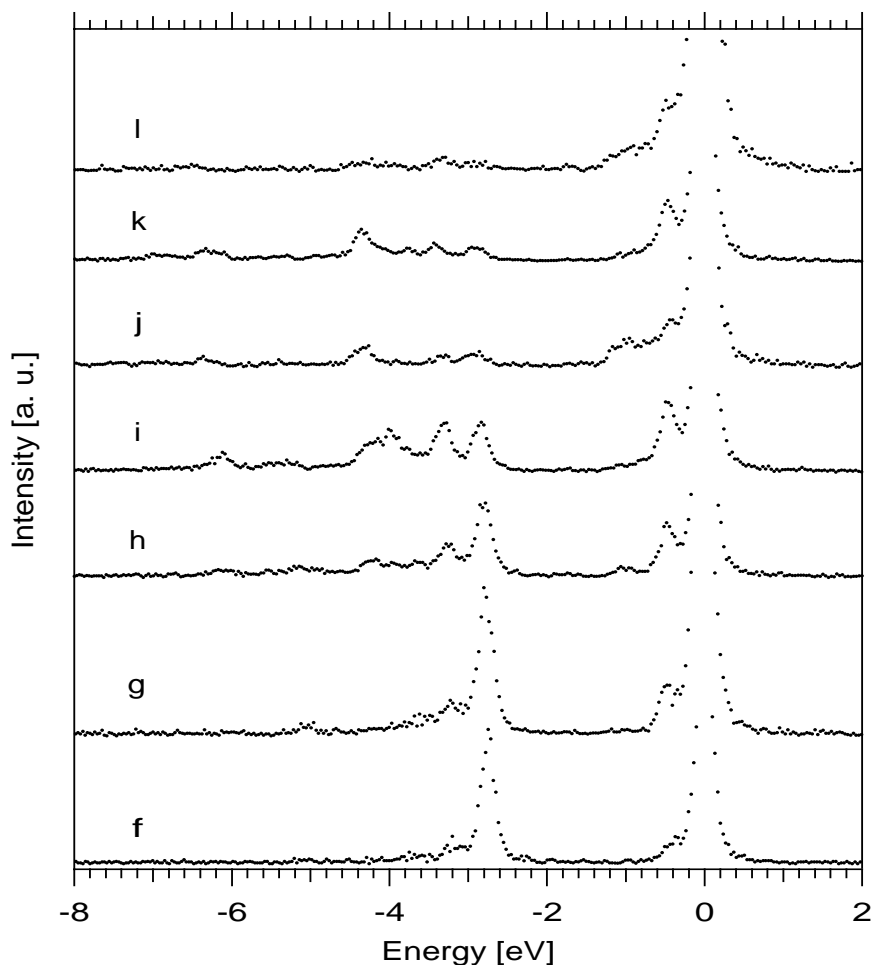
Figure 2. Enlarged inelastic x-ray scattering part of the resonant Dy 4f → 4d spectra from DyF$_3$.

J =11/2 components in the ground state of DyF$_3$. Indications of other extra-structures missing from atomic calculations can be seen in the energy range between -2.0 and -1.2 eV, as in spectra l and m. However, the present level of statistics does not permit identification.

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